

# PATENT ABSTRACTS OF JAPAN

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(54) FUEL CELL ELECTRODE USING POROUS CARBON FILM, FILM- ELECTRODE BONDED BODY AND FUEL CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a fuel cell electrode having a carrier structure capable of effectively utilizing a noble metal based catalyst and using a simple process to make it, a film-electrode bonded body and a fuel cell.

SOLUTION: A noble metal particulate is carried and carbon particulates are filled in the very fine hole of a porous carbon film having a very fine communicating hole to form this fuel cell electrode. The fuel cell electrode is bonded on both sides of a high polymer electrolyte film to form this film-electrode bonded body (sometimes written as MEA for short). This fuel cell has the film-electrode bonded body as a component.

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**CLAIMS**

[Claim(s)]

[Claim 1] The electrode for fuel cells which a noble-metals particle is supported and comes to fill up a carbon particle in the micropore of the porous carbon film which has a detailed free passage hole.

[Claim 2] The electrode for fuel cells according to claim 1 whose void content an average aperture is 25 – 85% in 0.05–10 micrometers for a porous carbon film.

[Claim 3] The electrode for fuel cells according to claim 1 with which a porous carbon film gives a functional group to the front face, and hydrophilization is carried out.

[Claim 4] The electrode for fuel cells according to claim 1 whose porous carbon film is what has the thickness of 3–100 micrometers.

[Claim 5] The electrode for fuel cells according to claim 1 with which noble metals are supported with 0.1 – 40% of the weight of the rate in the electrode.

[Claim 6] The film-electrode zygote which comes to join the electrode for fuel cells according to claim 1 to 5 to the both sides of the polyelectrolyte film.

[Claim 7] The fuel cell which has a film-electrode zygote according to claim 6 as a component.

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**DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Field of the Invention] the electrode for fuel cells with which this invention used the porous carbon film, and a film-electrode zygote -- and it is alike and is related with a fuel cell.

[0002]

[Description of the Prior Art] In recent years, development and utilization of a fuel cell are progressing. For example, in the case of a solid-state polyelectrolyte mold fuel cell, the porous carbon plate which consists of a carbon fiber paper-making object with a thickness of 0.1-0.3mm is formed, the gas diffusion electrode which made the front face support the platinum system catalyst as an electrode catalyst is joined to the both sides of a solid polymer electrolyte layer, the separator which consists of a substantia-compacta carbon plate with a thickness of 1-3mm to which the gas-passageway slot was attached is formed in the outside of the porous carbon plate of both sides, and the cell is constituted. Moreover, in the case of a phosphoric acid fuel cell, the porous carbon plate which consists of a carbon fiber paper-making object with a thickness of 0.1-0.3mm is formed, the gas diffusion electrode which made the front face support the platinum system catalyst as an electrode catalyst is joined to the both sides of an electrolyte layer which made the phosphoric acid hold to a phosphoric-acid supporter, the separator with a thickness of 1-3mm to which the gas-passageway slot was attached is formed in the outside of the porous carbon plate of both sides, and the cell is constituted.

[0003] Conventionally, as a carbon ingredient of noble-metals system catalyst support, the ingredient of the shape of powder represented by carbon black is used, and the electrode which is the component of the reaction section of a polymer electrolyte fuel cell is also produced using the paste which consists of the carbon powder and binders, such as resin, with which noble metals were supported, and a solvent (for example, JP,5-36418,A etc.). However, it was difficult to form the support structure where structure control of the electrode produced since powder is used as a start raw material has a limit, and an expensive noble-metals system catalyst can be used effectively.

[0004] Moreover, in order to change internal resistance and to make it operate stably because the wastewater in the cell under generation of electrical energy is overdue, various measures are required for an edge strip. For this reason, although securing reactant gas, electronic conduction pass, and a generation water discharge path by compounding a carbon fiber and a carbon particle is proposed, a creation process is complicated, the pole diameter and thickness of a component have a limit and there are few degrees of freedom of a design.

[0005]

[Problem(s) to be Solved by the Invention] This invention aims at having the support structure where a noble-metals system catalyst can be used effectively, and obtaining the electrode for fuel cells with a simple making process, a film-electrode zygote, and a fuel cell.

[0006]

[Means for Solving the Problem] A noble-metals particle is supported in the micropore of the porous carbon film which has a detailed free passage hole, and this invention relates to the electrode for fuel cells which comes to fill up a carbon particle. Moreover, this invention relates to the film-electrode zygote (it may be written as MEA) which comes to join the aforementioned electrode for fuel cells to the both sides of the polyelectrolyte film. Furthermore, this invention relates to the fuel cell which has the aforementioned film-electrode zygote as a component.

[0007]

[Embodiment of the Invention] The desirable mode of this invention is listed below.

- 1) The above-mentioned electrode for fuel cells whose void content an average aperture is 25 - 85% in 0.05-10 micrometers for a porous carbon film.
- 2) The above-mentioned electrode for fuel cells with which a porous carbon film gives a functional group to the front face, and hydrophilization is carried out.
- 3) The above-mentioned electrode for fuel cells whose porous carbon film is what has the thickness of 3-100 micrometers.

4) The above-mentioned electrode for fuel cells with which noble metals are supported with 0.1 – 40% of the weight of the rate in the electrode.

[0008] The porous carbon film in this invention has the vesicular structure which has a detailed free passage hole, an average aperture is [ a void content ] 25 – 85% in 0.05–10 micrometers suitably, and especially thickness is 3–100 micrometers. Especially the aforementioned porous carbon film has the vesicular structure which has a detailed free passage hole, and consists of the carbon film structure with smooth front faces other than an open hole.

[0009] Between the pores by which pore is the so-called open hole which continued to other front faces, and adjoins the shape of a path has wall-like structure from the front face of arbitration, and the porosity film which has a detailed free passage hole in this specification means the film which has the structure prolonged in nonlinear, while pore is crooked. The conceptual diagram of a vesicular structure which has this detailed free passage hole is shown in drawing 1 .

[0010] That is, since said porous carbon film will be led to the pore of the shape of a path prolonged in nonlinear and a \*\* style will be carried out in nonlinear if gas is passed, a short pass does not happen. Furthermore, parts other than the open hole which pore was prolonged out of the film, arrived at the front face, and formed the front face of a porous carbon film with the vesicular structure in this invention are smooth sides, and when a laminating is carried out to the carbon structure of multilayer structure, a separator, etc., an interface with other layers becomes field contact according to said smooth side.

[0011] Since front faces other than an open hole have smooth nature, the carbon film structure of the porous carbon film in this invention becomes field contact in an interface, when a layered product is formed.

[0012] Furthermore, 0.05–10 micrometers of average apertures of the carbon film structure of the porous carbon film in this invention are 0.05–2 micrometers preferably. In under the range of the above [ a surface average aperture ], since it will become difficult for gas to become easy to flow linearly, to cover the large range, and to carry out the \*\* style of the gas to homogeneity if it stops being able to carry out the \*\* style of the gas efficiently and an average aperture crosses the above-mentioned range, since a pressure loss arises, it is not suitable.

[0013] Moreover, the void content of the carbon film structure of a porous carbon film is 30 – 70% preferably 25 to 85%. In under the range of the above [ a void content ], since the mechanical strength of an electrode will become small if \*\*\*\*\* of gas decreases and a void content crosses the above-mentioned range, it is not desirable. Moreover, it is suitable for the carbon film structure of the above and a porous carbon film that the rate of graphitization is 90% or more especially preferably 30% or more preferably 10% or more. Since the mechanical strength of an electrode will become high and flexibility will improve if it is desirable and becomes especially 90% or more, since conductivity and thermal conductivity will become higher than the electrode which consists of common carbon powder if the rate of graphitization becomes 30% or more, it is more suitable, and it is \*\*.

[0014] The porous carbon film in this invention has the vesicular structure which has a detailed free passage hole, and front faces other than an open hole can carry out the heating carbonization of the smooth high thermal-resistance polymer film under an anaerobic ambient atmosphere, and can manufacture it suitably. Since a vesicular structure can be held when the high thermal-resistance polymer was used and it heats, it is desirable.

[0015] Said high thermal-resistance polymer will not be especially limited, if the vesicular structure which consists of a detailed free passage hole can be held even if it is possible to form the porous membrane which has a detailed free passage hole and it carries out heating carbonization. Although polymers, such as a polyimide system, a cellulose system, a furfural resin system, and a phenol resin system, can be mentioned suitably, since a carbonization reaction advances in the state of solid phase and a mechanical strength can obtain the high carbon structure easily by heating carbonization, especially aromatic polyimide is suitable. The polyamic acid which is the precursor of aromatic polyimide, and the polyamic acid imide-ized partially are also included in aromatic polyimide here.

[0016] It can have the vesicular structure which has said detailed free passage hole, and the high thermal-resistance polymer film with smooth front faces other than an open hole can be suitably manufactured by the phase converting method using a polymer solution. The solution which dissolved the polymer in the organic solvent (solvent) can be cast for example, on a support substrate, and it can obtain by the so-called phase converting method which forms pore using the phase separation phenomenon produced in order that a polymer may be immersed in an insoluble organic solvent, water, etc. by having compatibility (non-solvent) and a solvent and a non-solvent may permute the flow casting film by said organic solvent in that case. However, by the phase converting method applied in order to obtain a demarcation membrane, a compact layer is made on a front face.

[0017] While the flow casting film of a smooth polymer solution is formed, and a front face next makes the front face of this flow casting film carry out the laminating of the solvent permutation speed-regulation material (porous film), subsequently contacts the layered product to a non-solvent and forms pore by phase separation

suitable first, the porosity polymer film is deposited. Since the front face (front faces other than an aperture) of the porosity polymer film formed by this approach holds the surface smooth nature of the original flow casting film, the porosity polymer film with smooth front faces other than an open hole can be easily obtained with the vesicular structure which has a free passage hole.

[0018] When front faces other than an open hole carry out the heating carbonization of the smooth high thermal-resistance polymer film under an anaerobic ambient atmosphere with the vesicular structure which has a detailed free passage hole, the carbon film structure with smooth front faces other than an open hole can be obtained with the vesicular structure which has a detailed free passage hole. Although especially an anaerobic ambient atmosphere is not limited, the inside of inert gas, such as nitrogen gas, argon gas, and gaseous helium, and a vacuum is suitable for it. Since a decomposition product may dissipate, or a carbon content may distill off and carbon yield may become low when a temperature up is carried out rapidly, as for heating carbonization, a structure defect also tends to be made preferably. Therefore, as for especially a programming rate, it is desirable to carry out a temperature up and to carbonize gradually hereafter, by 20-degree-C/, at about 1-10 degrees C/minute in sufficiently late rate. As long as sufficient carbonization is performed, what kind of temperature and time amount are sufficient as whenever [stoving temperature], or heating time. Moreover, especially in order to raise the rate of graphitization of the carbon structure obtained and to make a mechanical strength, conductivity, and thermal conductivity high, the range of 2600-3000 degrees C is desirable, and 1200-3500 degrees C of things held for 20 - 180 minutes in said temperature requirement are suitable.

[0019] Moreover, if it pressurizes at the time of heating in the case of said heating carbonization, since the rate of graphitization can be raised and the carbon film structure with high conductivity and thermal conductivity with a high and mechanical strength can be obtained, it is desirable. Since change of the configuration accompanying the contraction under heating carbonization etc. is suppressed, or the stacking tendency of the carbon part currently carbonized is raised and graphitization is promoted by pressurization, the carbon film structure with high mechanical strength, conductivity, and thermal conductivity can be obtained. As for a pressure, it is desirable to add during heat treatment in the temperature field which the carbon film structure does not contract, and especially the pressure is good to impress in the magnitude of 10-250MPa one to 250 MPa. Although the 1 shaft pressurization elevated-temperature furnace generally used can perform pressurization, since the risk at which the carbon film structure breaks in the case of pressurization is mitigable if a hot-pressing machine and isotropic pressure hot pressing (HIP) are used, it is carried out especially suitably.

[0020] Moreover, in order to promote graphitization, the compound which has the effectiveness which promotes graphitization of a boron compound etc. beforehand on the high thermal-resistance polymer film with the vesicular structure which has the detailed free passage hole to heat may be added. Furthermore, if the heating carbonization of the layered product to which front faces other than an open hole carried out two or more sheet laminating of the smooth high thermal-resistance polymer film with the vesicular structure which has a detailed free passage hole is carried out, it can carbonize and unify and the porous carbon film in this invention can be obtained. By this approach, since the porous carbon film of various thickness can be obtained from the thin polymer film, in case the porous carbon film which has the film thickness of 50 micrometers or more especially is produced, it is used especially suitably.

[0021] In this invention, it can consider as the porous carbon film by which gave the functional group and hydrophilization was carried out to the front face by carrying out grade processing of the aforementioned porous carbon film for 1 - 200 minutes by the oxidation-treatment agent which consists of mixture with inorganic acids, such as permanganates, such as a functional-group grant processing agent, for example, potassium permanganate, or permanganic acid NATORIMU, a sulfuric acid, or a nitric acid. Since catalyst support and electrolytic coating can be made easy by performing hydrophilization processing, it is suitable.

[0022] The electrode for fuel cells of this invention has the aforementioned detailed free passage hole, and is obtained by supporting a noble-metals particle and being filled up with a carbon particle in the micropore of the porous carbon film whose parts other than an open hole are smooth sides.

[0023] Either one sort chosen from the group which consists of palladium, platinum, a rhodium, a ruthenium, and iridium as said noble metals and the alloy of these matter, each combination or combination with other transition metals is mentioned. Mean particle diameter is 5nm or less, and, as for the magnitude of a noble-metals particle, it is desirable that the maximum particle diameter is 15nm or less.

[0024] In this invention, that with which said noble-metals particle was supported by carbon particles, such as carbon black, is used as a catalyst. The noble-metals particle in this invention is supported, and what contains 10 % of the weight - 60 % of the weight for noble metals is suitable for a carbon particle.

[0025] Although the amount of support of the aforementioned noble-metals particle changes in this invention with the property required of the fuel cell produced using that electrode and the film thickness of an electrode layer, and specific surface area It converts into per unit area of an electrode. In a positive electrode Two or more 0.02 mg/cm, Two or less 0.45 mg/cm, it is especially desirable to be used in a two or less 0.25 mg/cm amount also two or less 0.35 mg/cm and in it, and it is desirable to be used in a two or less 0.25 mg/cm amount

two or more [ 0.01mg //cm ] especially on a membranous negative electrode. Moreover, in this invention, it is desirable for a noble-metals particle to be supported and to use together a polyelectrolyte or an oligomer electrolyte (ionomer) with a carbon particle. As for a polyelectrolyte or especially an oligomer electrolyte, it is desirable in that case that they are two or less 3 mg/cm also two or less 5 mg/cm and in it two or more 0.1 mg/cm and two or less 10 mg/cm per unit area of an electrode.

[0026] the approach which the electrode for fuel cells of this invention applies to the whole one side surface or the predetermined configuration of a porous carbon film the catalyst constituent which the aforementioned noble-metals particle is supported [ constituent ] and made the solvent carry out homogeneity distribution of a polyelectrolyte or the oligomer electrolyte (ionomer) by the carbon particle and the case, is dried suitably, and a noble-metals particle is supported in micropore, and is filled up with a carbon particle -- it is obtained. By the aforementioned approach, a part of interior of a porous carbon film may be filled up with a catalyst constituent, and you may fill up with it over total thickness. The concept of the electrode for fuel cells obtained is shown in drawing 2 . Thus, when a catalyst support carbon particle accumulates in the continuation hole of porous carbon, the structure ( drawing 3 ) where the space of mass transfer was secured and the electron and the conduction path of a proton were built can be acquired easily.

[0027] The polymer or oligomer of arbitration which produces the polymer or oligomer which reacts as an aforementioned polyelectrolyte or an aforementioned oligomer electrolyte with the polymer with ionic conductivity of arbitration, oligomer, an acid, or a base, and has ionic conductivity can be mentioned. As a suitable polyelectrolyte or an oligomer electrolyte, the fluoropolymers which have pendant ion exchange groups, such as a sulfonic group, with the gestalt of a proton or a salt, for example, sulfonic-acid fluoropolymers, for example, the Nafion film, (Du Pont trademark), sulfonic-acid fluoro oligomer, sulfonation polyimide, sulfonation oligomer, etc. are mentioned. An aforementioned polyelectrolyte or an aforementioned oligomer electrolyte needs to be insolubility in water substantially at the temperature of 100 degrees C or less.

[0028] As a suitable solvent used for manufacture of the aforementioned catalyst constituent ink, polar solvents, such as one to C6 alcohol, a glycerol, ethylene carbonate, propylene carbonate, BUCHIRUKA-BONE-TO, an ethylene carbamate, a propylene carbamate, a butylene carbamate, an acetone, an acetonitrile, dimethylformamide, dimethylacetamide, a 1-methyl-2-pyrrolidone, difluoro benzene, and a sulfolane, are mentioned. An organic solvent may be used independently and may be used as mixed liquor with water again. As for an organic solvent, it is desirable to use it especially 1% or more on the basis of the weight of a constituent in 3% or more and 70% or less of amount. Moreover, as for the operating rate in the case of using the mixed liquor of an organic solvent and water, it is desirable that organic solvent:water is within the limits of 10:1-1:3 in a volume ratio.

[0029] The film-electrode zygote of this invention is obtained by being about 1-100kg/cm<sup>2</sup> in pressure, and carrying out the grade hotpress of the electrode for fuel cells which is the above, and is made and obtained for 0.1 - 30 minutes at the temperature of 120-150 degrees C, suitably, at the both sides of the polyelectrolyte film. The polymer or oligomer of arbitration which produces the polymer or oligomer which reacts as the aforementioned polyelectrolyte film with the polymer with the above-mentioned ionic conductivity of arbitration, oligomer, an acid, or a base, and has ionic conductivity can be mentioned.

[0030] Moreover, since one side of an electrode needs to have an electrolyte membrane and a good adhesive property as above-mentioned, it is desirable to coat with the polyelectrolyte or the oligomer electrolyte beforehand. Moreover, since the field of the opposite side needs to form electronic conduction pass in contact with a gaseous diffusion layer or a separator with a \*\* style function, not coating with the polyelectrolyte or the oligomer electrolyte is desirable. The electrode of such a gestalt can be attained by using positively the phenomenon in which a solution interface retreats in the solvent evaporation direction of for example, catalyst constituent ink.

[0031] Since the film-electrode zygote of this invention has many detailed free passage holes, it is suitable as the structure of a high performance fuel cell which can offer the reaction place of the cell reaction widely distributed to homogeneity. Moreover, by using the carbon powder which can perform support of catalyst noble metals easily, the electrode structure which harnessed the features which a porous carbon film has can be produced simple, and it is useful. Furthermore, since the electrode structure consists of two kinds of configuration members of the carbon particle (powder) with which the porous carbon film and the noble-metals particle were supported, the degree of freedom of the design for processing the water inside an electrode can be extended by making each member into a hydrophilic property or hydrophobicity.

[0032] The fuel cell of this invention uses a film-electrode zygote as a component, and uses the aforementioned film-electrode zygote for an oxygen side with much generating of water suitably. The aforementioned film-electrode zygote or other various film-electrode zygotes (it is also called the film-electrode structure) are used for a hydrogen side (fuel side). For example, it is obtained by arranging respectively the seal for preventing the leakage of reactant gas for the separator of a pair between the separators of this pair through a direct or gaseous diffusion layer on both sides of an electrode.

[0033]

[Example] Next, when aromatic polyimide suitable as a high thermal-resistance polymer is used about this invention, an intermediary's example explains. However, this invention is not limited to the following examples. In addition, in this invention, the performance evaluation of air permeability, a void content, an average aperture, the rate of graphitization, and a fuel cell was measured by the following approach.

[0034] \*\* Air permeability JIS It measured according to P8117. B mold gar Leh DENSOME-TA - (Oriental energy machine company make) was used as a measuring device. The film of a sample is bound tight to the circular hole of 2 the diameter of 28.6mm, and an area of 645mm, and the air in a cylinder is passed out of a cylinder from the trial circular hole section with the container liner weight of 567g. The time amount which 100 cc of air passes was measured, and it considered as air permeability (gar Leh value).

[0035] \*\* The thickness, area, and weight of the film cut off in void content predetermined magnitude were measured, and the void content was calculated by the degree type from eyes weight. The weight and D to which the film surface product measured S of a degree type, and thickness and w measured d are a consistency, and polyimide computed the consistency for every sample about 1.34 and the carbon film structure in consideration of the rate of graphitization for which it asked by the approach of mentioning later.

Void content  $= (1 - W / (S \times d \times D)) \times 100$  [0036] \*\* the scanning electron microscope photograph of an average aperture film front face -- photographing -- opening of 50 or more points -- a hole -- area -- measuring -- this hole -- the degree type from the average of area -- following -- a hole -- it asked for the average diameter at the time of presupposing that a configuration is a perfect circle from count. Sa of a degree type means the average of hole area.

the rate X diffraction of average aperture  $= 2 \times (S_a / \pi)^{1/2}$  \*\* graphitization -- measuring -- Ruland -- it asked by law.

[0037] \*\* It asked for the thickness of the thickness porous carbon film of a porous carbon film by scanning microscope observation of the film thickness gage of a contact process, and a cross section.

\*\* TEM and SEM observation estimated the magnitude of the noble-metals particle distributed to the magnitude electrode of a noble-metals particle.

[0038] \*\* Using the electronic load equipment for performance-evaluation fuel cells of a fuel cell, the fuel gas pressure inside a cel was made into 0.1MPa(s) and the cell temperature of 80 degrees C, it generated electricity by performing humidification of fuel gas through 70-degree C HABURA -, and the current-voltage characteristic was measured.

\*\* It asked for the series resistance component in operating the series resistance component measurement fuel cell in a fuel cell cel by 40mA constant current, intercepting a current momentarily, and incorporating and analyzing the electrical potential difference in that case by the time amount wave.

[0039] The manufacture 3 of an example of reference 1 porosity polyimide film, 3', and the polyamic acid solution that carried out the polymerization of 4, and 4'-biphenyl tetracarboxylic dianhydride and a p phenylenediamine, and obtained them in the N-methyl-2-pyrrolidone are cast on a stainless plate. A flow casting film front face is covered by the polyolefine fine porosity film (air permeability 550 seconds /, and 100 cc) (you pore UP2015 by Ube Industries, Ltd.) which is solvent permutation speed-regulation material. It was immersed into 1-propanol and the polyamic acid film with smooth front faces other than an open hole was deposited with the vesicular structure which has a detailed free passage hole. Subsequently, after being underwater immersed for 10 minutes, it exfoliated from the stainless plate, and in the condition of having fixed to pin tenter -, temperature of 400 degrees C and heat treatment during 20 minutes were performed in air, and the porosity polyimide film was obtained. The rate of imide-izing was 70%, and this film was 27 micrometer [ of thickness ], and air permeability 360 seconds /, 100 cc, 48% of void contents, and 0.17 micrometers of average apertures.

[0040] The porosity polyimide film of \*\*\*\*\* of the electrode using an example 1 porous-carbon film was carbonized at the temperature of 1400 degrees C under the nitrogen gas air current, and the porous carbon film of rate [ of 18% ] of graphitization, film thickness [ of 21 micrometers ], and air permeability 380 seconds /, 100ml, 45% of void contents, and 0.13 micrometers of average apertures was obtained. Predetermined time immersion of this was carried out into the mixed water solution of potassium permanganate and a 35-% of the weight nitric acid, and the front face of a carbon film was made to generate functional groups, such as a hydroxyl group and a carboxyl group. After that, with 70-degree C distilled water, it washed enough repeatedly and dried.

[0041] 10ml [ of water ] and isopropanol 20ml and 0.05g (5 % of the weight, dimethylformamide/water = 1/1, Du Pont) of commercial Nafion 5012 solutions were stirred and mixed for 50mg (20 % of the weight of platinum, made in [ U.S. ] Johnson Massey) of platinum support carbon catalysts in the ice bath, after predetermined time, ultrasonic irradiation of this mixture was carried out for 1 hour, and the particle was decentralized. Thus, one side of the above-mentioned porous carbon-ized film of 5cm angle was plastered with the obtained catalyst distribution constituent, it dried, and the gas diffusion electrode was obtained. The amount of platinum in the obtained gas diffusion electrode was 0.20 mg/cm<sup>2</sup> per electrode unit area, as a result of carrying out a quantum by the ICP AEM method.

[0042] 10ml [ of water ] and isopropanol 20ml and 0.05g (5 % of the weight, Du Pont) of commercial Nafion 5012 solutions were stirred and mixed with example of reference 2 carbon powder for 100mg (20 % of the weight of platinum, made in [ U.S. ] Johnson Massey) of production platinum support carbon catalysts of the electrode using carbon paper in the ice bath, after predetermined time, ultrasonic irradiation of this mixture was carried out for 1 hour, and the particle was decentralized. Thus, one side of the carbon paper (Toray Industries, Inc. make) of 5cm angle was plastered with the obtained catalyst distribution constituent, it dried, and the gas diffusion electrode was obtained. The amount of platinum in the obtained gas diffusion electrode was 0.4 mg/cm<sup>2</sup> per electrode unit area, as a result of carrying out a quantum by the ICP AEM method.

[0043] Nafion 1135 film (Du Pont make) which is an example 2 film-electrode zygote (MEA) and production polyelectrolyte film of a fuel cell -- 3% hydrogen-peroxide-solution solution -- continuing -- the inside of 3% sulfuric-acid water solution -- warming -- it processed. On the gas diffusion electrode obtained in the example 1, 100mg of Nafion 5012 solutions was applied, it dried 5%, and the catalyst support electrode pore front face was covered with the ultra-thin polyelectrolyte layer. Moreover, the gas diffusion electrode obtained in the example 2 of reference was similarly covered with the ultra-thin polyelectrolyte. The gas diffusion electrode was arranged so that the reaction aspect which is a catalyst support electrode pore front face might counter the both sides of Nafion 1135 film which is polyelectrolyte film in two obtained electrodes, the pressure welding was carried out using the hotpress machine the condition for 135 degrees C, 5kg/cm<sup>2</sup>, and 10 - 12 minutes, and MEA was obtained. Using this MEA, with the conventional method, it put with the separator plate and the fuel cell was produced.

[0044] The electrode side which produced fuel gas (hydrogen) in the example 2 of reference to the fuel electrode of a cell was supplied using the obtained fuel cell, and the porous carbon film electrode side which produced air in the example 1 to the air pole was supplied. The pressure inside a cel was supplied by about 0.1 MPa(s), was made into the cell temperature of 80 degrees C, and performed humidification of gas through 70-degree C HABURA -. When the current-voltage characteristic was measured for constant current every other hour with the sink, repeatability showed the good current-voltage characteristic over the long time ( drawing 4 ). The magnitude of the series resistance component inside the cel at the time of constant current operation also operated with about 1 constant value ( drawing 5 ).

[0045] The gas diffusion electrode obtained in the example 3 example 1 was used for two poles, and also MEA was obtained like the example 2. The fuel cell was produced like the example 2 using this MEA. this fuel cell -- using -- the fuel electrode of a cell -- fuel gas (hydrogen) -- supplying -- an air pole -- air -- pressure [ inside a cel ]: -- it supplied by about 0.1 MPa(s), and considered as the cell temperature of 80 degrees C, and humidification of gas was performed through 70-degree C HABURA -. When the current-voltage characteristic was measured for constant current every other hour with the sink, repeatability showed the good current-voltage characteristic over the long time ( drawing 6 ). The magnitude of the series resistance component inside the cel at the time of constant current operation was also small, and the value also operated with about 1 constant value ( drawing 7 ).

[0046] The gas diffusion electrode obtained in the example 2 of example of comparison 1 reference was used for two poles, and also MEA was obtained like the example 2, and the fuel cell was produced like the example 2 using this MEA. this fuel cell -- using -- the fuel electrode of a cell -- fuel gas (hydrogen) -- supplying -- an air pole -- air -- pressure [ inside a cel ]: -- when it supplied by about 0.1 MPa(s), it considered as the cell temperature of 80 degrees C and humidification of gas was performed through 70-degree C HABURA -, in the relation between a current and an electrical potential difference, there is much dispersion ( drawing 8 ) and the magnitude of actuation and a series resistance component was unstable ( drawing 9 ). Moreover, the absolute value of a series resistance component was also large.

[0047]

[Effect of the Invention] According to this invention, the electrode which made the porous carbon film distribute the noble-metals particle of a desired amount can be obtained easily, it has the support structure where a noble-metals system catalyst can be used effectively, and the electrode for fuel cells and a film-electrode zygote can be obtained with a simple making process. Moreover, according to this invention, the fuel cell by which actuation was stabilized can be obtained.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is a conceptual diagram of a vesicular structure which has a detailed free passage hole.

[Drawing 2] Drawing 2 is the conceptual diagram of the electrode for fuel cells of this invention using the porous carbon film (porous carbon base material) in this invention.

[Drawing 3] Drawing 3 is the partial enlarged drawing of drawing 2.

[Drawing 4] Drawing 4 is the current-voltage characteristic about the fuel cell which used the electrode for fuel cells of an example 2 for the air pole.

[Drawing 5] Drawing 5 is a series resistance component at the time of constant current operation of the fuel cell which used the electrode for fuel cells of an example 2 for the air pole.

[Drawing 6] Drawing 6 is the current-voltage characteristic about the fuel cell which used the electrode for fuel cells of an example 3 for a hydrogen pole and the two poles of an air pole.

[Drawing 7] Drawing 7 is a series resistance component at the time of constant current operation of the fuel cell which used the electrode for fuel cells of an example 3 for a hydrogen pole and the two poles of an air pole.

[Drawing 8] Drawing 8 is the current-voltage characteristic about the fuel cell which used for a hydrogen pole and the two poles of an air pole the electrode which consists of the catalyst support carbon powder and carbon paper of the example 1 of a comparison.

[Drawing 9] Drawing 9 is a series resistance component at the time of constant current operation of the fuel cell which used for a hydrogen pole and the two poles of an air pole the electrode which consists of the catalyst support carbon powder and carbon paper of the example 1 of a comparison.

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最終頁に続く

(54) 【発明の名称】 多孔質炭素フィルムを用いた燃料電池用電極、膜-電極接合体及び燃料電池

(57) 【要約】

【課題】 貴金属系触媒を有効に利用できる担持体構造を有し作製工程がシンプルである燃料電池用電極、膜-電極接合体および燃料電池を得る。

【解決手段】 微細な連通孔を有する多孔質炭素フィルムの微細孔内に、貴金属微粒子が担持され炭素微粒子を充填してなる燃料電池用電極、前記の燃料電池用電極を高分子電解質膜の両側に接合してなる膜-電極接合体 (MEAと略記することもある。)、前記の膜-電極接合体を構成要素として有する燃料電池。

## 【特許請求の範囲】

【請求項 1】微細な連通孔を有する多孔質炭素フィルムの微細孔内に、貴金属微粒子が担持され炭素微粒子を充填してなる燃料電池用電極。

【請求項 2】多孔質炭素フィルムが、平均孔径が 0.05～10  $\mu\text{m}$  で空孔率が 25～85% である請求項 1 に記載の燃料電池用電極。

【請求項 3】多孔質炭素フィルムが、その表面に官能基を付与して親水化されたものである請求項 1 に記載の燃料電池用電極。

【請求項 4】多孔質炭素フィルムが、3～100  $\mu\text{m}$  の厚みを有するものである請求項 1 に記載の燃料電池用電極。

【請求項 5】貴金属が、電極中に 0.1～40 重量% の割合で担持されている請求項 1 に記載の燃料電池用電極。

【請求項 6】請求項 1～5 のいずれかに記載の燃料電池用電極を高分子電解質膜の両側に接合してなる膜-電極接合体。

【請求項 7】請求項 6 に記載の膜-電極接合体を構成要素として有する燃料電池。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】この発明は、多孔質炭素フィルムを用いた燃料電池用電極、膜-電極接合体及び燃料電池に関する。

## 【0002】

【従来の技術】近年、燃料電池の開発および実用化が進んでいる。例えば、固体高分子電解質型燃料電池の場合、厚さ 0.1～0.3 mm の炭素繊維抄紙体からなる多孔質炭素板を設け、その表面に電極触媒としての白金系触媒を担持させたガス拡散電極を高分子固体電解質層の両側に接合し、両側の多孔質炭素板の外側にガス流路溝の付いた厚さ 1～3 mm の緻密質炭素板からなるセパレータを設けて電池セルを構成している。また、リン酸型燃料電池の場合、厚さ 0.1～0.3 mm の炭素繊維抄紙体からなる多孔質炭素板を設け、その表面に電極触媒としての白金系触媒を担持させたガス拡散電極をリン酸保持体にリン酸を保持させた電解質層の両側に接合し、両側の多孔質炭素板の外側にガス流路溝の付いた厚さ 1～3 mm のセパレータを設けて電池セルを構成している。

【0003】従来、貴金属系触媒担持体のカーボン材料としては、カーボンブラックに代表される粉末状の材料が使用されており、固体高分子型燃料電池の反応部の構成材料である電極も、貴金属が担持されたカーボン粉末と樹脂などのバインダーと溶媒からなるペーストを用いて作製されている（例えば、特開平 5-36418 号公報など）。しかしながら、粉末を出発原料とするゆえに作製される電極の構造制御には制限があり、高価な貴金

属系触媒を有効に利用できる担持体構造を形成する事は困難であった。

【0004】また、発電中のセル内の排水が滞ることで内部抵抗が変動し、安定動作させるためには周辺部材に種々の施策が必要である。このため、炭素繊維と炭素粒子とを複合させることにより反応ガスと電子伝導パスおよび生成水排出経路を確保することが提案されているが、作成工程が複雑で構成材料の細孔径や厚みに制限があり設計の自由度が少ない。

## 10 【0005】

【発明が解決しようとする課題】この発明は、貴金属系触媒を有効に利用できる担持体構造を有し作製工程がシンプルである燃料電池用電極、膜-電極接合体および燃料電池を得ることを目的とする。

## 【0006】

【課題を解決するための手段】この発明は、微細な連通孔を有する多孔質炭素フィルムの微細孔内に、貴金属微粒子が担持され炭素微粒子を充填してなる燃料電池用電極に関する。また、この発明は、前記の燃料電池用電極を高分子電解質膜の両側に接合してなる膜-電極接合体（MEA と略記することもある。）に関する。さらに、この発明は、前記の膜-電極接合体を構成要素として有する燃料電池に関する。

## 【0007】

【発明の実施の形態】以下にこの発明の好ましい態様を列記する。

1) 多孔質炭素フィルムが、平均孔径が 0.05～10  $\mu\text{m}$  で空孔率が 25～85% である上記の燃料電池用電極。

20 2) 多孔質炭素フィルムが、その表面に官能基を付与して親水化されたものである上記の燃料電池用電極。

3) 多孔質炭素フィルムが、3～100  $\mu\text{m}$  の厚みを有するものである上記の燃料電池用電極。

4) 貴金属が、電極中に 0.1～40 重量% の割合で担持されている上記の燃料電池用電極。

【0008】この発明における多孔質炭素フィルムは、微細な連通孔を有する多孔質構造を持ち、好適には平均孔径が 0.05～10  $\mu\text{m}$  で空孔率が 25～85% であり、特に厚みが 3～100  $\mu\text{m}$  である。特に、前記の多孔質炭素フィルムは、微細な連通孔を有する多孔質構造を持ち、開放孔以外の表面が平滑な炭素膜構造体からなるものである。

【0009】この明細書において、微細な連通孔を有する多孔質フィルムとは、任意の表面から細孔が通路状に他の表面まで連続したいわゆる開放孔であって、隣接する細孔間が壁状構造になっており、且つ、細孔は屈曲しながら非直線的に延びた構造を有するフィルムをいう。この微細な連通孔を有する多孔質構造の概念図を図 1 に示す。

50 【0010】即ち、前記多孔質炭素フィルムは、ガスを

流すと非直線的に延びた通路状の細孔に導かれて非直線的に配流されるのでショートパスが起こらない。更に、この発明における多孔質構造を持つ多孔質炭素フィルムの表面は、細孔が膜内から延びて表面に達して形成した開放孔以外の部分が平滑面であり、多層構造の炭素構造体および/またはセパレータなどと積層したときに他の層との界面が前記平滑面によって面接触になるものである。

【0011】この発明における多孔質炭素フィルムの炭素膜構造体は、開放孔以外の表面が平滑性を持っているので、積層体を形成したときに界面において面接触になる。

【0012】更に、この発明における多孔質炭素フィルムの炭素膜構造体は、平均孔径が $0.05 \sim 10 \mu\text{m}$ 、好ましくは $0.05 \sim 2 \mu\text{m}$ である。表面の平均孔径が上記の範囲未満では圧損が生ずるのでガスを効率的に配流できなくなり、平均孔径が上記の範囲を越えるとガスが直線的に流れやすくなって広い範囲に亘ってガスを均一に配流することが難しくなるので好適ではない。

【0013】また、多孔質炭素フィルムの炭素膜構造体の空孔率は $25 \sim 85\%$ 、好ましくは $30 \sim 70\%$ である。空孔率が上記の範囲未満ではガスの配流量が少なくなり、空孔率が上記の範囲を越えると電極の機械的強度が小さくなるので好ましくない。また、前記、多孔質炭素フィルムの炭素膜構造体は、黒鉛化率が $10\%$ 以上、好ましくは $30\%$ 以上、特に好ましくは $90\%$ 以上であることが好適である。黒鉛化率が $30\%$ 以上になると導電性、熱伝導性が一般的な炭素粉末からなる電極より高くなるので好ましく、特に $90\%$ 以上になると電極の機械的強度が高くなり可撓性が向上するのでより好適である。

【0014】この発明における多孔質炭素フィルムは、微細な連通孔を有する多孔質構造を持ち、開放孔以外の表面が平滑な高耐熱性ポリマー膜を嫌気性雰囲気下で加熱炭化して好適に製造することができる。高耐熱性ポリマーを用いると加熱したときに多孔質構造を保持できるので好ましい。

【0015】前記高耐熱性ポリマーは、微細な連通孔を有する多孔質膜を形成することが可能で、かつ、加熱炭化しても微細な連通孔からなる多孔質構造を保持できるものであれば、特に限定するものではない。ポリイミド系、セルロース系、フルフラール樹脂系、フェノール樹脂系などのポリマーを好適に挙げることができるが、特に芳香族ポリイミドは加熱炭化によって固相の状態で炭素化反応が進行し、容易に機械的強度が高い炭素構造体を得ることができるので好適である。ここで芳香族ポリイミドには、芳香族ポリイミドの前駆体であるポリアミク酸、及び、部分的にイミド化したポリアミク酸も含む。

【0016】前記微細な連通孔を有する多孔質構造を持

ち、開放孔以外の表面が平滑な高耐熱性ポリマー膜は、ポリマー溶液を用いて相転換法によって好適に製造することができる。ポリマーを有機溶剤（溶媒）に溶解した溶液を、例えば支持基板上に流延し、その流延膜を前記有機溶剤とは相溶性を有しポリマーは不溶な有機溶剤や水など（非溶媒）に浸漬し、その際に溶媒と非溶媒とが置換するために生じる相分離現象を利用して細孔を形成するいわゆる相転換法によって得ることができる。しかし分離膜を得るために適用される相転換法では表面に緻密層ができる。

【0017】好適には、まず表面が平滑なポリマー溶液の流延膜を形成し、次に該流延膜の表面に溶媒置換速度調整材（多孔性フィルム）を積層させ、次いでその積層体を非溶媒と接触させて相分離によって細孔を形成しながら多孔質ポリマー膜を析出させる。この方法で形成された多孔質ポリマー膜の表面（開孔部以外の表面）は元の流延膜の表面平滑性を保持するので、連通孔を有する多孔質構造を持ち開放孔以外の表面が平滑な多孔質ポリマー膜を容易に得ることができる。

【0018】微細な連通孔を有する多孔質構造を持ち開放孔以外の表面が平滑な高耐熱性ポリマー膜を嫌気性雰囲気下で加熱炭化することによって、微細な連通孔を有する多孔質構造を持ち開放孔以外の表面が平滑な炭素膜構造体を得ることができる。嫌気性雰囲気は、特に限定しないが、窒素ガス、アルゴンガス、ヘリウムガスなどの不活性ガス中か、真空中が好適である。加熱炭化は、急激に昇温すると分解物が散逸したり炭素分が留去して炭素収率が低くなることがあるので好ましくなく構造欠陥もでやすい。そのために昇温速度は $20^\circ\text{C}/\text{分}$ 以下、特に $1 \sim 10^\circ\text{C}/\text{分}$ 程度の十分遅い速度で昇温して徐々に炭化するのが好ましい。加熱温度や加熱時間は十分な炭化がおこなわれればどんな温度や時間でも構わない。また、得られる炭素構造体の黒鉛化率を高めて機械的強度や導電性や熱伝導性を高くするためには $1200 \sim 3500^\circ\text{C}$ 、特に $2600 \sim 3000^\circ\text{C}$ の範囲が好ましく、前記温度範囲で $20 \sim 180$ 分間保持することが好適である。

【0019】また、前記加熱炭化の際に加熱時に加圧すると、黒鉛化率を高めて機械的強度が高く且つ導電性及び熱伝導性が高い炭素膜構造体を得ることができるので好ましい。加圧によって、加熱炭化中の収縮などに伴う形状の変化を抑えたり、炭素化されつつある炭素部分の配向性を高めて黒鉛化が促進されるので、機械的強度、導電性、熱伝導性が高い炭素膜構造体を得ることができる。圧力は、熱処理中に炭素膜構造体が収縮しない温度領域で付加することが好ましく、その圧力は $1 \sim 250 \text{MPa}$ 、特に $10 \sim 250 \text{MPa}$ の大きさで印加するのがよい。加圧は一般的に用いられる一軸加圧高温炉で行うことができるが、高温圧縮機や等方圧熱間プレス（HIP）を用いると加圧の際に炭素膜構造体が壊れる

リスクを軽減できるので特に好適におこなわれる。

【0020】また、黒鉛化を促進するために、加熱する微細な連通孔を有する多孔質構造を持つ高耐熱性ポリマー膜に予めホウ素化合物などの黒鉛化を促進する効果を有する化合物を添加してもよい。さらに、微細な連通孔を有する多孔質構造を持ち開放孔以外の表面が平滑な高耐熱性ポリマー膜を複数枚積層した積層体を加熱炭化すると、炭化し且つ一体化して本発明における多孔質炭素フィルムを得ることができる。この方法では、薄いポリマー膜から種々の膜厚の多孔質炭素フィルムを得ることができるので、特に50 $\mu$ m以上の膜厚みを有する多孔質炭素フィルムを作製する際に特に好適に用いられる。

【0021】この発明においては、前記の多孔質炭素フィルムを官能基付与処理剤、例えば過マンガン酸カリウムあるいは過マンガン酸ナトリウムなどの過マンガン酸塩と硫酸あるいは硝酸などの無機酸との混合物からなる酸化処理剤によって1~200分間程度処理することで、表面に官能基を付与して親水化された多孔質炭素フィルムとすることができる。親水化処理を行うことで触媒担持及び電解質のコーティングを容易にすることができるので好適である。

【0022】この発明の燃料電池用電極は、前記の微細な連通孔を有し開放孔以外の部分が平滑面である多孔質炭素フィルムの微細孔内に、貴金属微粒子が担持され炭素微粒子を充填することによって得られる。

【0023】前記貴金属としては、パラジウム、白金、ロジウム、ルテニウムおよびイリジウムよりなる群から選ばれる1種、及びこれらの物質の合金、各々の組合せ又は他の遷移金属との組合せのいずれかが挙げられる。貴金属微粒子の大きさは、平均粒子径が5nm以下で、最大粒子径が15nm以下であることが好ましい。

【0024】この発明においては、前記貴金属粒子がカーボンブラック等の炭素微粒子に担持されたものが触媒として使用される。この発明における貴金属微粒子が担持され炭素微粒子は、貴金属を10重量%~60重量%を含むものが好適である。

【0025】この発明において、前記の貴金属粒子の担持量は、その電極を用いて作製される燃料電池に要求される特性および電極膜の膜厚み、比表面積によって異なってくるが、電極の単位面積あたりに換算して、正極では0.02mg/cm<sup>2</sup>以上、0.45mg/cm<sup>2</sup>以下、特に0.35mg/cm<sup>2</sup>以下、中でも0.25mg/cm<sup>2</sup>以下の量で使用されることが好ましく、膜の負極上では0.01mg/cm<sup>2</sup>以上、特に0.25mg/cm<sup>2</sup>以下の量で使用されることが好ましい。また、この発明において、貴金属微粒子が担持され炭素微粒子とともに高分子電解質あるいはオリゴマー電解質（イオノマー）を併用することが好ましい。その際、高分子電解質あるいはオリゴマー電解質は、電極の単位面積あたりで0.1mg/cm<sup>2</sup>以上、10mg/cm<sup>2</sup>

以下、特に5mg/cm<sup>2</sup>以下、中でも3mg/cm<sup>2</sup>以下であることが好ましい。

【0026】この発明の燃料電池用電極は、好適には前記の貴金属微粒子が担持され炭素微粒子および場合により高分子電解質あるいはオリゴマー電解質（イオノマー）を溶媒に均一分散させた触媒組成物を多孔質炭素フィルムの片面全面あるいは所定形状に塗布、乾燥して、微細孔内に貴金属微粒子が担持され炭素微粒子を充填する方法によって得られる。前記の方法によって、触媒組成物は多孔質炭素フィルムの内部の一部に充填されてもよく全厚みに渡って充填されてもよい。得られる燃料電池用電極の概念を図2に示す。このように、触媒担持炭素微粒子が多孔質炭素の連通孔内に堆積されることにより、物質移動の空間が確保されかつ電子およびプロトンの伝導経路が構築された構造（図3）を容易に得ることができる。

【0027】前記の高分子電解質あるいはオリゴマー電解質としては、イオン伝導度をもつ任意のポリマー又はオリゴマー、又は酸又は塩基と反応してイオン伝導度をもつポリマー又はオリゴマーを生ずる任意のポリマー又はオリゴマーを挙げることができる。適当な高分子電解質あるいはオリゴマー電解質としては、プロトン又は塩の形態でスルホン酸基等のペンダントイオン交換基を持つフルオロポリマー、例えばスルホン酸フルオロポリマー例えばナフィオン膜（デュボン社登録商標）、スルホン酸フルオロオリゴマーやスルホン化ポリイミド、スルホン化オリゴマー等が挙げられる。前記の高分子電解質あるいはオリゴマー電解質は100℃以下の温度で実質的に水に不溶性であることが必要である。

【0028】前記の触媒組成物インクの製造に使用される適当な溶媒としては、C1-6アルコール、グリセリン、エチレンカーボネート、プロピレンカーボネート、ブチルカーボネート、エチレンカルバメート、プロピレンカルバメート、ブチレンカルバメート、アセトン、アセトニトリル、ジメチルホルムアミド、ジメチルアセトアミド、1-メチル-2-ピロリドン、ジフルオロベンゼン及びスルホラン等の極性溶媒が挙げられる。有機溶媒は単独で使用してもよくまた水との混合液として使用してもよい。有機溶媒は、組成物の重量を基準にして、1%以上、特に3%以上、そして70%以下の量で使用することが好ましい。また、有機溶媒と水との混合液を使用する場合の使用割合は、体積比で有機溶媒：水が10：1~1：3の範囲内であることが好ましい。

【0029】この発明の膜-電極接合体は、前記のようにして得られる燃料電池用電極を高分子電解質膜の両側に、好適には120~150℃の温度で1~100kg/cm<sup>2</sup>程度の圧力で、0.1~30分間程度ホットプレスすることによって得られる。前記の高分子電解質膜としては、前述の、イオン伝導度をもつ任意のポリマー又はオリゴマー、又は酸又は塩基と反応してイオン伝導

度をもつポリマー又はオリゴマーを生ずる任意のポリマー又はオリゴマーを挙げることができる。

【0030】また、上述の通り、電極の片面は電解質膜と良好な接着性を持つことが必要であるので、予め高分子電解質またはオリゴマー電解質がコーティングされていることが好ましい。また、反対側の面はガス拡散層または配流機能付きセパレータと接して電子伝導パスを形成する必要があるために、高分子電解質またはオリゴマー電解質がコーティングされていないことが好ましい。このような形態の電極は、例えば触媒組成物インクの溶媒蒸発方向に溶液界面が後退する現象を積極的に利用することで達成することができる。

【0031】この発明の膜-電極接合体は、微細な連通孔を多数持っているので、広く均一に分散した電池反応の反応場を提供することができる高性能燃料電池の構造体として好適なものである。また、触媒貴金属の担持が容易にできる炭素粉末を用いることによって、多孔質炭素フィルムの持つ特長を活かした電極構造体を簡便に作製することができ有益である。さらに、電極構造体が多孔質炭素フィルムと貴金属微粒子が担持された炭素微粒子（粉末）の2種類の構成部材からなるので、各々の部材を親水性もしくは疎水性にすることによって、電極内部の水の処理を行うための設計の自由度を広げることができる。

【0032】この発明の燃料電池は、膜-電極接合体を構成要素とし、好適には水の発生が多い酸素側に前記の膜-電極接合体を使用し、水素側（燃料側）には前記の膜-電極接合体あるいは他の種々の膜-電極接合体（膜-電極構造体ともいう）を使用し、例えば電極の両側に直接あるいはガス拡散層を介して一対のセパレータを、該一対のセパレータ間に反応ガスの漏れを防止するためのシールを各々配設することによって得られる。

#### 【0033】

【実施例】次に、この発明について、高耐熱性ポリマーとして好適な芳香族ポリイミドを使用した場合につての実施例で説明する。但し、本発明は以下の実施例に限定されるものではない。尚、本発明において、透気度、空孔率、平均孔径、黒鉛化率、燃料電池の性能評価は次の方法によって測定した。

#### 【0034】①透気度

JIS P8117に準じて測定した。測定装置としてB型ガーレーデンソメーター（東洋精機社製）を使用した。試料の膜を直径28.6mm、面積645mm<sup>2</sup>の円孔に締付け、内筒重量567gにより、筒内の空気を試験円孔部から筒外へ通過させる。空気100ccが通過する時間を測定し、透気度（ガーレー値）とした。

#### 【0035】②空孔率

所定の大きさに切取った膜の膜厚、面積及び重量を測定し、目付重量から次式により空孔率を求めた。次式のSは膜面積、dは膜厚、wは測定した重量、Dは密度であ

りポリイミドは1.34、炭素膜構造体については後述する方法で求めた黒鉛化率を考慮して試料ごとに密度を算出した。

$$\text{空孔率} = (1 - W / (S \times d \times D)) \times 100$$

#### 【0036】③平均孔径

膜表面の走査型電子顕微鏡写真を撮り、50点以上の開口部について孔面積を測定し、該孔面積の平均値から次式に従って孔形状が真円であるとした際の平均直径を計算より求めた。次式のS<sub>a</sub>は孔面積の平均値を意味する。

$$\text{平均孔径} = 2 \times (S_a / \pi)^{1/2}$$

#### ④黒鉛化率

X線回折を測定しRuland法により求めた。

#### 【0037】⑤多孔質炭素フィルムの厚み

多孔質炭素フィルムの厚みは、接触式の膜厚み計および断面の走査型顕微鏡観察により求めた。

#### ⑥貴金属粒子の大きさ

電極に分散した貴金属微粒子の大きさは、TEM及びSEM観察によって評価した。

#### 【0038】⑦燃料電池の性能評価

燃料電池用電子負荷装置を用いて、セル内部の燃料ガス圧力を0.1MPa、電池温度80℃とし、燃料ガスの加湿を70℃のハブラーを介して行うことで発電を行い、電流-電圧特性を測定した。

#### ⑧燃料電池セル内の直列抵抗成分測定

燃料電池を40mAの定電流で運転しておき、瞬間的に電流を遮断してその際の電圧を時間波形で取り込み解析することで、直列抵抗成分を求めた。

#### 【0039】参考例1

#### 多孔質ポリイミドフィルムの製造

3, 3', 4, 4'-ビフェニルテトラカルボン酸二無水物とパラフェニレンジアミンとをN-メチル-2-ピロリドン中で重合して得たポリアミック酸溶液をステンレス板上に流延し、流延膜表面を溶媒置換速度調整材である透気度550秒/100ccのポリオレフィン微多孔膜（宇部興産社製ユーポアUP2015）で覆い、1-プロパノール中に浸漬し、微細な連通孔を有する多孔質構造を持ち開放孔以外の表面が平滑なポリアミック酸膜を析出させた。次いで、水中に10分間浸漬したあとで、ステンレス板から剥離し、ピンテンターに固定した状態で、空気中にて温度400℃、20分間熱処理をおこなって、多孔質ポリイミドフィルムを得た。このフィルムは、イミド化率が70%であり、膜厚27μm、透気度360秒/100cc、空孔率48%、平均孔径0.17μmであった。

#### 【0040】実施例1

#### 多孔質炭素フィルムを用いた電極の作製

この多孔質ポリイミドフィルムを窒素ガス気流下1400℃の温度で炭素化して、黒鉛化率18%、膜厚み21μm、透気度380秒/100ml、空孔率45%、平

均孔径  $0.13 \mu\text{m}$  の多孔質炭素フィルムを得た。これを、過マンガン酸カリウムおよび 35 重量%硝酸の混合水溶液中に所定時間浸漬して、炭素フィルムの表面に水酸基やカルボキシル基等の官能基を生成させた。その後  $70^\circ\text{C}$  の蒸留水で繰り返し充分洗浄して乾燥した。

【0041】白金担持カーボン触媒（白金 20 重量%、米国のジョンソン・マッセイ社製）50 mg を水 10 ml、イソプロパノール 20 ml、および市販ナフィオン 5012 溶液（5 重量%、ジメチルホルムアミド/水 = 1/1、デュボン社）0.05 g を氷浴中で攪拌・混合し、所定時間後、該混合物を 1 時間超音波照射して粒子の分散化を行った。このようにして得られた触媒分散組成物を 5 cm 角の上記多孔質炭素化フィルムの片面に塗着、乾燥してガス拡散電極を得た。得られたガス拡散電極中の白金量は ICP 発光分析法にて定量した結果、電極単位面積当り  $0.20 \text{ mg/cm}^2$  であった。

#### 【0042】参考例 2

炭素粉末とカーボンペーパーを用いた電極の作製  
白金担持カーボン触媒（白金 20 重量%、米国のジョンソン・マッセイ社製）100 mg を水 10 ml、イソプロパノール 20 ml、および市販ナフィオン 5012 溶液（5 重量%、デュボン社）0.05 g を氷浴中で攪拌・混合し、所定時間後、該混合物を 1 時間超音波照射して粒子の分散化を行った。このようにして得られた触媒分散組成物を 5 cm 角のカーボンペーパー（東レ社製）の片面に塗着、乾燥してガス拡散電極を得た。得られたガス拡散電極中の白金量は ICP 発光分析法にて定量した結果、電極単位面積当り  $0.4 \text{ mg/cm}^2$  であった。

#### 【0043】実施例 2

膜-電極接合体 (MEA) および燃料電池の作製  
高分子電解質膜であるナフィオン 1135 膜（デュボン社製）を 3% 過酸化水素水溶液、続いて 3% 硫酸水溶液中にて加温処理した。実施例 1 で得られたガス拡散電極上に 5% ナフィオン 5012 溶液 100 mg を塗布、乾燥して、触媒担持電極細孔表面を極薄高分子電解質層で被覆した。また、参考例 2 で得られたガス拡散電極を同様にして極薄高分子電解質で被覆した。得られた 2 つの電極を高分子電解質膜であるナフィオン 1135 膜の両側に触媒担持電極細孔表面である反応部面が対向するようにガス拡散電極を配し、 $135^\circ\text{C}$ 、 $5 \text{ kg/cm}^2$ 、10~12 分間の条件でホットプレス機を用いて圧接して MEA を得た。この MEA を用いて常法によってセパレート板で挟み込み、燃料電池を作製した。

【0044】得られた燃料電池を用いて、電池の燃料極に燃料ガス（水素）を参考例 2 で作製した電極側に供給し、空気極に空気を実施例 1 で作製した多孔質炭素フィルム電極側に供給した。セル内部の圧力は約  $0.1 \text{ MPa}$  で供給し、電池温度  $80^\circ\text{C}$  とし、ガスの加湿を  $70^\circ\text{C}$  のハブラーを介して行った。定電流を流しながら 1 時間

おきに電流-電圧特性を測定したところ、長時間に渡って再現性が良い電流-電圧特性を示した（図 4）。定電流運転時のセル内部の直列抵抗成分の大きさもほぼ一定値で動作した（図 5）。

#### 【0045】実施例 3

実施例 1 で得られたガス拡散電極を両極に用いた他は実施例 2 と同様にして、MEA を得た。この MEA を用いて実施例 2 と同様にして、燃料電池を作製した。この燃料電池を用いて、電池の燃料極に燃料ガス（水素）を供給し、空気極に空気をセル内部の圧力：約  $0.1 \text{ MPa}$  で供給し、電池温度  $80^\circ\text{C}$  とし、ガスの加湿を  $70^\circ\text{C}$  のハブラーを介して行った。定電流を流しながら 1 時間おきに電流-電圧特性を測定したところ、長時間に渡って再現性が良い電流-電圧特性を示した（図 6）。定電流運転時のセル内部の直列抵抗成分の大きさも小さく、値もほぼ一定値で動作した（図 7）。

#### 【0046】比較例 1

参考例 2 で得られたガス拡散電極を両極に用いた他は実施例 2 と同様にして、MEA を得て、この MEA を用いて実施例 2 と同様にして、燃料電池を作製した。この燃料電池を用いて、電池の燃料極に燃料ガス（水素）を供給し、空気極には空気をセル内部の圧力：約  $0.1 \text{ MPa}$  で供給し、電池温度  $80^\circ\text{C}$  とし、ガスの加湿を  $70^\circ\text{C}$  のハブラーを介して行ったところ、電流と電圧との関係にばらつきが多く（図 8）、動作および直列抵抗成分の大きさが不安定であった（図 9）。また、直列抵抗成分の絶対値も大きかった。

#### 【0047】

【発明の効果】この発明によれば、多孔質炭素フィルムに所望の量の貴金属粒子を分散させた電極を容易に得ることができ、貴金属系触媒を有効に利用できる担持体構造を有しシンプルな作製工程によって燃料電池用電極、膜-電極接合体を得ることができる。また、この発明によれば、動作が安定した燃料電池を得ることができる。

#### 【図面の簡単な説明】

【図 1】図 1 は、微細な連通孔を有する多孔質構造の概念図である。

【図 2】図 2 は、この発明における多孔質炭素フィルム（多孔質炭素基材）を用いたこの発明の燃料電池用電極の概念図である。

【図 3】図 3 は、図 2 の部分拡大図である。

【図 4】図 4 は、実施例 2 の燃料電池用電極を空気極に用いた燃料電池についての電流-電圧特性である。

【図 5】図 5 は、実施例 2 の燃料電池用電極を空気極に用いた燃料電池の定電流運転時の直列抵抗成分である。

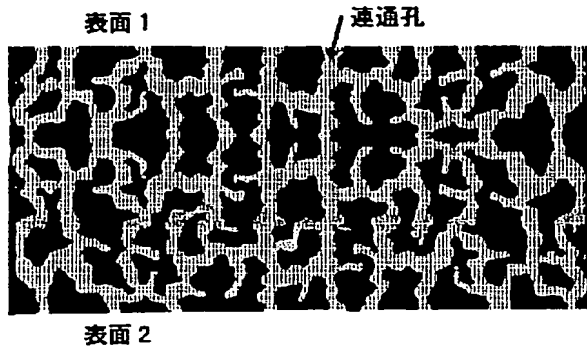
【図 6】図 6 は、実施例 3 の燃料電池用電極を水素極および空気極の両極に用いた燃料電池についての電流-電圧特性である。

【図 7】図 7 は、実施例 3 の燃料電池用電極を水素極および空気極の両極に用いた燃料電池の定電流運転時の直

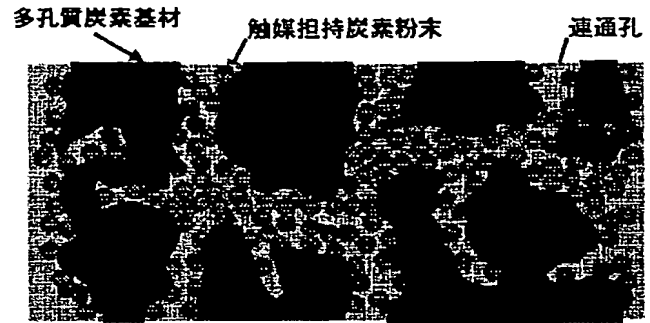
列抵抗成分である。

【図8】図8は、比較例1の触媒担持炭素粉末とカーボンペーパーとからなる電極を水素極および空気極の両極に用いた燃料電池についての電流-電圧特性である。

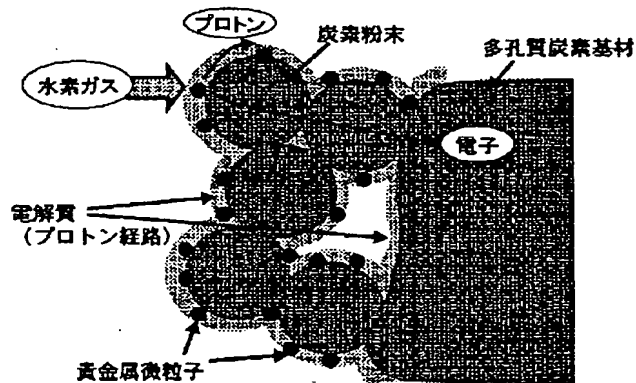
【図1】



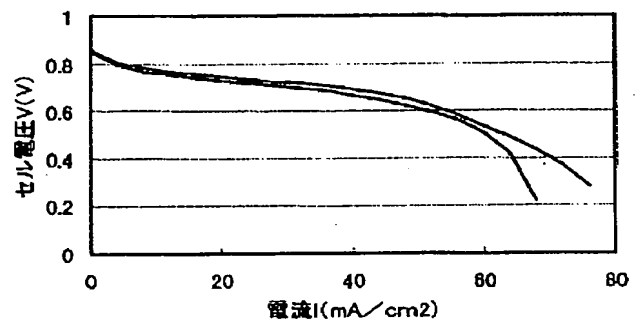
【図2】



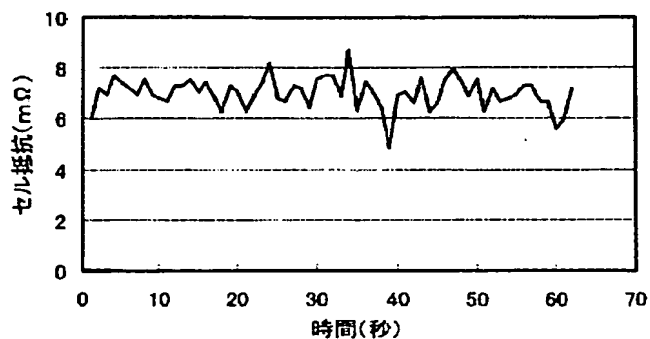
【図3】



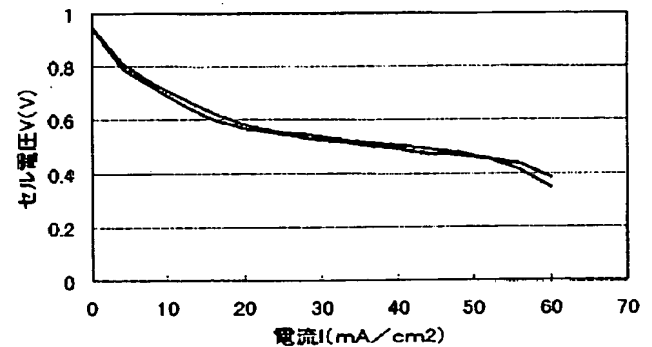
【図4】



【図5】

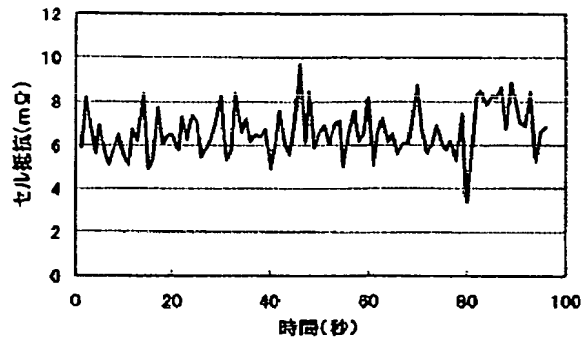


【図6】

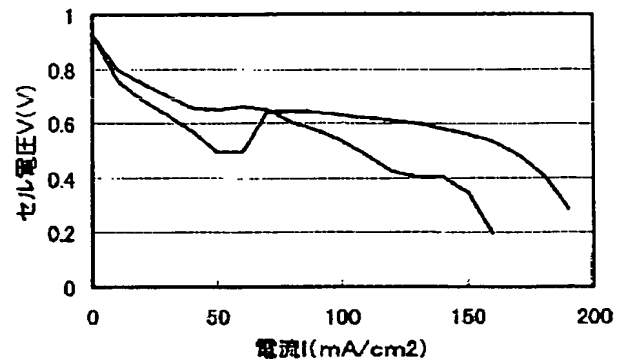




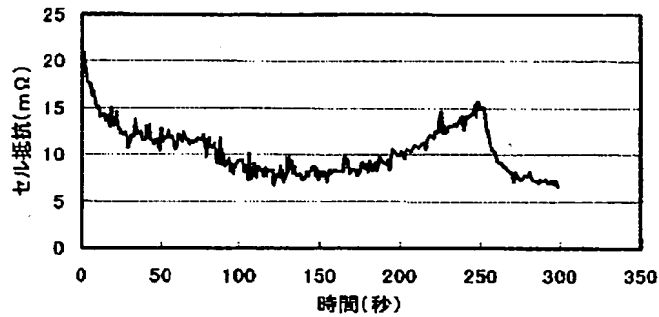
【図7】



【図8】



【図9】



フロントページの続き

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